Article

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Environmentally benign synthesis methods of zero valent iron nanoparticles

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KEYWORDS

green synthesis, nZVI, dehalogenation, VOCl, field test

ABSTRACT

Zero valent iron nanoparticles (nZVI) have already proven their efficacy in the reductive disposal of a wide array of environmental contaminants in numerous laboratory and field trials. However, their large-scale application in remediation applications is hindered by the high costs and the legislative issues associated with the conventional nZVI synthesis method that relies on $NaBH_4$ as a reducing agent. The two common strategies to replace sodium borohydride are (i) totally "green" nZVI syntheses based on plant extracts, and (ii) "semi-green" nZVI synthesis based on less toxic and more cost-effective industrial chemical reducing agents. In this paper we present a comparative evaluation of green and semi-green synthesis methods. The former utilized coffee, green tea and Virginia creeper (Parthenocissus tricuspidata) leave extracts, the latters were based on sodium dithionite and sodium borohydride. nZVI synthesis was done in untreated tap water at room temperature to reduce the environmental footprint of the process. nZVI performance was assessed on the basis of time-dependent oxidation/reduction potential measurements and also by the reductive dehalogenation of volatile chlorinated organics in groundwater samples from an actual field test.

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INTRODUCTION

Nanotechnology in environmental remediation is a field gaining increasing momentum due to its capacity to reduce production costs and to improve the efficiency of the remediation process.[1] Nanoremediation means the utilization of highly reactive nanoscale materials for the elimination of pollutants and the purification of air, water or ground bodies through chemical reduction or catalytic processes.[2–5] Zero-valent nanoparticulate iron (nZVI) is a well-known aggressive reducing agent[6,7] used often in the treatment of soil and groundwater contaminated by e.g. halogenated hydrocarbons[8] or heavy metals[9]. According to Li et al. there are two nZVI synthesis strategies[10]: top-down methods include the decomposition of iron compounds[11], vacuum-sputtering[12] and ball-milling[10], whereas bottom-up methods promote the growth of the nanoparticles by chemical synthesis, usually through the reaction of Fe^{2+} or Fe^{3+} salts with sodium borohydride. The main limitations of top-down methods are the high operational costs, the need for special equipment and the low nZVI yield. On the other hand, bottom-up methods often make use of sodium borohydride. $NaBH_4$ is an expensive and dangerous chemical that yields oxidized boron species during nZVI synthesis that cannot be easily separated from the nZVI product even though they are strictly prohibited from entering groundwater bodies in several countries. Therefore, low cost, environmentally benign, scalable iron nanoparticle synthesis methods are heavily sought after today.

Sodium dithionite can be used to reduce Fe(II) and produce nZVI at high pH in the presence of oxygen.[13,14] $Na_2S_2O_4$ is less expensive and toxic than $NaBH_4$, is readily available in large quantities, its reaction with iron ions does not generate any hydrogen and the reaction products are among the least dangerous chemicals. Moreover, it can also restore the reducing capacity of passivated nZVI.[13] It is expected that the reaction of sodium dithionite with ferrous sulphate could result in a favorable nZVI production process because $FeSO_4$ itself is also a non-toxic, easily available iron source. Besides the utilization of low impact chemicals, this reaction is considered "semi-green" mostly because of its insensitivity to oxygen, which allows the usage of unpurified tap water and eliminates the need for additional deoxygenation technologies (e.g. N_2 bubbling) and pressure bearing vessels. Consequently, the resulting technology has a low environmental footprint and is a good candidate for the scalable field production of nZVI with an "Open Air" technology.

"Green" alternatives to conventional nanoparticle synthesis methods have been gaining popularity in the past two decades and Prof. Rajender S. Varma has contributed very

significantly to this field.[2,15–19] It is the use of natural product extracts and the elimination of high temperature and/or pressure reaction steps that makes a production route green and cost effective. The active ingredients of the natural product extracts can be polyphenols and flavonoids from coffee, tea and wine, proteins and vitamins.[18,20,21] These components are non-toxic, biodegradable and can act as reducing and capping agents, thus promoting the formation and inhibiting the agglomeration of nanoparticles.[20] The mechanism of metal ion reduction to nanoparticles by plant extracts has been elucidated for the Au^{+}-dihydromyricetin[22] and the Ag^{+}–hydrolysable tannin[23] pairs earlier. Metal ions are complexed by the phenolic OH groups and then reduced to metal while the biomolecule assumes its oxidized ascorbic acid form. In a typical synthesis the extract is mixed with a metal salt solution at near ambient temperature and nanoparticles form spontaneously in a timeframe ranging from a few minutes up to one day, depending on the metal – extract pair used. Both the reactivity and the diameter distribution of the produced nanoparticles depend on the type of extract used as that determines which reducing and capping agents are present in the synthesis mixture. It is also noteworthy that the conjugated π-electron system of polyphenols and flavonoids allows the donation of electrons from the hydroxyl groups to free radicals, therefore, they can exhibit antioxidant activity and thus prolong the lifetime of nZVI sols[24]. By chelating metal ions flavonoids inhibit Fenton and Haber-Weiss reactions[25] and they remain active free radical scavengers even in there complex form[26].

Previous attempts at the green synthesis of nZVI were successful with many different natural reducing agents, e.g. green tea extract[27], eucalyptus leaf extract[5], citrine juice[28], Ulmus davidiana bark extract[29], Lawsonia inermis and Gardenia jasminoides leaf extract[30] and many different fruit tree leaf extracts including passion fruit, cherry, apricot, avocado, orange etc.[31] However, it has been shown that the reduction of Fe^{3+} ions with herb extracts is seldom complete[32] and that the efficiency of fully green nZVI in the degradation of organic compounds tends to be below 70%.[3] Combining the process with Fenton like oxidation can improve the efficiency significantly.[33,34] Summarizing, green nZVI production for remediation applications is very inviting from the sustainable chemistry point of view. However, the maturity of the currently available green synthesis methods makes it necessary to investigate further scalable iron nanoparticle production techniques as well.

Four possible reactions need to be considered when assessing the safety of applying nZVI for environmental remediation with perchloro-ethylene (PCE) as a model contaminant. These are (i) reductive dehalogenation (stepwise substitution of halogen atoms by hydrogen),

(ii) β-elimination (elimination of two halogen atoms from neighboring carbons), (iii) hydrogenation (addition of hydrogen to a double or triple carbon–carbon bond) and (iv) dehydrohalogenation (elimination of a hydrogen-halogenide and formation of a carbon–carbon bond. The latter two processes are responsible for the interconversions of degradation intermediates. It is known that 70-90% of all PCE is destroyed by β-elimination when using nZVI, thus the main intermediates are dichloro-acetylene and acetylene. These are further converted into trans-1,2-dichoro-ethylene and ethylene and finally into mineralized chlorine, ethylene and small carboxylic acids and alcohols. The latter two are readily biodegradable by microorganisms. Summarizing, the intermediates involved in nZVI-based volatile chlorinated organic remediation are not more unsafe than the starting material, whereas the end products are definitely safer both from the human and from the environmental point of view.

In this paper we compare the performance of sodium borohydride and sodium dithionite derived semi-green nZVI with that of iron nanoparticles obtained by totally green methods using green tea, coffee and Virginia creeper extracts. The novelties of the work are (i) the strictly room temperature and open air nZVI syntheses, (ii) the first use of Virginia creeper extract in this reaction and (iii) the use of actual groundwater samples collected from a chlorinated hydrocarbon contaminated industrial area to test the remediation efficiency of the synthesized nZVI sols and (iv) characterizing the best nZVI material in a field scale test.

EXPERIMENTAL

Synthesis

Virginia creeper (Parthenocissus quinquefolia, also known as Victoria creeper) leaves (VC) were collected locally (from the wall of the "Béke" building of the University of Szeged), washed thoroughly with deionized water to eliminate surface dust and dried at room temperature until their weight became constant at ambient conditions. The extract was prepared by boiling 5 g dry VC leaves in 100 mL deionized water at 80 °C for 80 minutes, thereafter the extracts were vacuum-filtered and stored at 4 °C for further use. A similar process was employed for the green tea (GT) and coffee (C) extracts except that the purchased dry tea leaves (Twinings™ of London, Green Tea&Lemon) and coffee (Tchibo Family) were boiled directly without any pretreatment. VC-Fe, C-Fe and GT-Fe labelled "green" nZVI

materials were synthesized by adding the corresponding extracts to 0.10 M aqueous $FeCl_3$*6 H_2O (97%, Sigma-Aldrich) solution (prepared using normal, untreated tap water) in a 1:1 volume ratio at room temperature and constantly stirring for 24 hours.

Semi-green synthesis methods utilized technical grade ferric chloride, ferrous chloride, ferrous sulfate, NaOH, sodium borohydride and sodium dithionite from Sigma-Aldrich. All chemicals were dissolved in untreated tap water in calculated amounts that ensured nZVI concentrations of 2500, 5000 and 10000 ppm in the final product sol after reaction[14,35,36]. First NaOH was added to the iron salt solution and the solution was stirred for 10 minutes. Then the reducing agent $Na_2S_2O_4$ or $NaBH_4$ was added and stirring was continued until the solution became completely black (5 min in the former, 40 min in the latter case). nZVI samples made from $FeCl_2$ by using $Na_2S_2O_4$ or $NaBH_4$ and labelled HG1-Fe and HG2-Fe, respectively. HG3-Fe was a reference sample made by reducing $FeCl_3$ with $NaBH_4$ and HG4-Fe was the product of reducing $FeSO_4$ with $Na_2S_2O_4$.

For laboratory tests and TEM analysis the as-prepared Fe nanoparticles were collected by vacuum filtration, quickly rinsed three times with deionized water and ethanol and finally re-suspended in untreated tap water. The field test was performed using the as-synthesized nZVI sol directly.

Characterization

Oxidation/reduction potential (ORP) values of 1000 ppm nZVI sols were measured on a Consort-C533 unit using a Consort-SK10B type ORP probe. Transmission Electron Microscopy (TEM) images were recorded at x180000 magnification and 125 pm/pixel resolution using a FEI Tecnai G2 20 X-Twin microscope operated at 200 kV. Powder X-ray diffractograms were recorded using a Rigaku Miniflex 2 unit operating with Cu Kα radiation. Energy dispersive X-ray spectroscopy (EDS) was performed by a Röntec spectrometer mounted on the column of a Hitachi S-4700 scanning electron microscope.

The general reducing ability of nZVI samples was characterized by measuring the amount of H_2 gas evolved when mixing 5000 ppm nZVI sols with concentrated sulphuric acid used in excess. The acid was added to the nZVI sol through a membrane-sealed opening of a round-bottom flask by a syringe. Mixing by a magnetic stirrer was maintained for 15 minutes. The amount of H_2 was measured by a calibrated gas burette after the reaction stopped and the system reached pressure equilibrium.

The efficiency of the nZVI samples in the environmentally relevant reductive dehalogenation of chlorinated volatile organic compounds (VOCl) was tested by mixing a chosen concentration nZVI sol in a predetermined excess amount to an actual contaminated groundwater sample at room temperature. The mixtures were kept in open vessels in stray ambient light at room temperature without stirring to simulate field conditions and analyzed by ORP measurement and gas chromatography (Shimadzu GCMS-QP2010 SE using a 30 m long 0.25 mm diameter ZBWax-Plus column with He carrier gas). Groundwater samples were obtained from a 12 m deep monitoring well established at an abandoned industrial site on the Great Hungarian Plain. The site used to be a service station that utilized lots of degreasing solvents, therefore, the full groundwater body is contaminated there with a mixture of VOCl molecules. The summed total concentration of PCE (perchloroethene), TCE (trichloroethene), DCE (1,2-dichloroethene) and VC (chloroethene) at this site was 3237 $\mu g \cdot dm^{-3}$.

RESULTS AND DISCUSSION

Particle size analysis

Characteristic TEM images of iron nanoparticles obtained by green and semi-green synthesis methods are presented in Figure 1. C-Fe and GT-Fe were practically indistinguishable, therefore, only GT-Fe is shown here. The average particle diameter was 124.2±31.8 nm for C-Fe and 119.6±25.8 nm for GT-Fe. Particles in the other five nZVI samples averaged below 100 nm in diameter: 47.5±8.8 nm for VC-Fe and 70.9±7.0, 23.5±4.1, 25.2±3.5 and 19.7±2.2 nm for HG1-Fe, HG2-Fe, HG3-Fe and HG4-Fe, respectively. The width of the particle diameter distribution curve was similar in all seven cases, with the standard deviation of particle diameter ranging from 11% to 26% of the mean. No TEM apparent impurities were observed in any of the samples. All seven iron nanoparticle samples exhibited isotropic morphology. HG3-Fe and HG4-Fe are characterized by sharp edges, corners and a generally triangular shape, while the other five particle types are more rounded.

XXX Insert Figure 1 here please XXX

Since the synthesis was performed in untreated tap water, it is theoretically possible that some of the synthesized nanoparticles were actually bimetallic, consisting of iron and a second metal reduced from tap water impurities. On the other hand, the quality of tap water in Hungary is regulated by the 201/2001 (X.25.) government directive that enforces strict limits

on the allowed metal ion contents of drinking water. Moreover, water in our region is of particularly high quality as determined by the continuous monitoring activities of the municipal waterworks. The annual average (and maximum) concentration of metallic impurities in 2013 was the following: Fe 0.114 (0.231) ppm, Mn 0.034 (0.047) ppm, As 0.007 (0.009) ppm, Na 38.11 (44.10) ppm, K 1.25 (1.30) ppm, Sb 0.20 (1.95) ppb, Al 9.36 (22.00) ppb, Hg 0.20 (0.66) ppb, Ni 0.28 (1.60) ppb, Se 0.17 (1.21) ppb, Pb 0.50 (5.30) ppb, Cu 0.005 (0.011) ppm, Cr 0.03 (0.17) ppb, Cd 0.00 (0.01) ppb. Our own EDS analysis was unable to identify any metals other than iron in the synthesized nZVI samples, which is in agreement with the expectations based on the approx. 1 atom% detection limit of the spectrometer and the low concentration of metallic impurities in tap water. Summarizing, it seems safe to assume that even if some bimetallic nanoparticles were formed during the nZVI synthesis from iron and metallic impurities, their amount relative to pure iron nanoparticles must have been so low that their effect can safely be neglected from the practical point of view.

Oxidation/reduction potential (ORP) measurements

Previous studies have suggested that the ORP of nZVI sols is a good indicator of their reductive dehalogenation efficiency.[37] The ORP values of all semi-green and green 1000 ppm nZVI sols are presented in the left panel of Figure 2. as a function of time. The error bars indicate the standard deviation of the ORP as calculated from five independent experiments.

XXX Insert Figure 2 here please XXX

Iron nanoparticles produced by using plant extracts featured ORP values in the -100 mV to -250 mV range immediately after synthesis, then their reduction potential decreased as a linear function of time. Letting the nZVI synthesis reaction run for 36 or 48 hours instead of 24 h did not change the starting ORP values. Fe nanoparticles synthesized with green tea extract and coffee offered the best and the worst ORP values among the green samples, respectively. Although it is somewhat surprising that Virginia creeper extract outperformed coffee extract, this can be explained by (i) the high antioxidant content of the former[38] and (ii) the possibility of picking a coffee brand which chanced to be lower than average on antioxidants. The ORP values of nZVI sols of semi-green origin were lower than those of the green ones (except for the poorly performing HG1-Fe) and also increased with time. The best initial ORP results were measured for HG2-Fe and HG3-Fe in agreement with received literature wisdom[33,39]. However, these were also the samples that lost their reduction potential

at the fastest rate in the long run. Sample HG4-Fe offered a balanced performance, combining the third best initial ORP value with a linear loss of reduction potential.

The right panel of Figure 2. presents the ORP vs. time functions of nZVI samples mixed with 1 equivalent of VOCl containing groundwater samples obtained from an actual contaminated site. The rapid initial decrease of the reduction potential in all seven cases is a clear indication of the dehalogenation reaction between the iron nanoparticles and the VOCls. The dehalogenation activity of nZVI synthesized using coffee and green tea extracts confirms earlier literature results, whereas that of Virginia creeper extract derived iron nanoparticles is reported here for the first time. The saturation of the curve indicates the practical endpoint of the reaction. As expected, samples with better initial reduction potential were able to remain active longer. Whereas C-Fe lost its reducing ability within 3 hours, samples HG2-Fe, HG3-Fe and HG4-Fe remained active for at least 24 hours. It is interesting to observe that these are exactly the three samples with the smallest average iron nanoparticle diameters (see TEM analysis above). Smaller nanoparticle size implies larger specific surface area and consequently, more active sites for both VOCl deterioration and the dissolved oxygen induced oxidative deactivation of the nZVI particle. Apparently, these detrimental effects are overcompensated by the large number and high activity of the small iron nanoparticles in these three cases.

H_2 evolution test and XRD characterization

The amount of H_2 released in the reaction of sulphuric acid with semi-green nZVI samples HG1-4 was measured both in field conditions (untreated tap water) and in solutions thoroughly deoxygenized by 1 hour of N_2 bubbling. Raw results were converted to nZVI efficiency percentage, where 100% efficiency means that all of the iron present in the system reacted stoichiometrically with the acid, that is, all iron was in the Fe^0 state. Results are presented in Figure 3.

XXX Insert Figure 3 here please XXX

The results are in agreement with the ORP findings insofar as samples HG2-Fe and HG3-Fe offered the best efficiencies in both series. However, it is worth noting that HG4-Fe proved to be the most robust material, because the performance difference between the oxygen-free and the field conditions was the smallest for this sol.

Powder X-ray diffractograms of these samples are presented in Figure 4. Peaks at 45° and 65° can be assigned to the (11) and (200) reflections of metallic iron, respectively. As expected from the previously described findings, these features are most pronounced for the HG2-Fe and HG3-Fe samples. The minor peaks in the diffractograms are due to iron-oxide phases. In agreement with the H_2 evolution experiments, samples HG4-Fe and HG1-Fe exhibited the best and the worst oxidation tolerance, respectively.

XXX Insert Figure 4 here please XXX

Quantitative VOCl deterioration measurements

The rapid loss of reducing ability ruled out the green nZVI samples from further consideration for a field test. Therefore, laboratory tests were continued with iron nanoparticles of semi-green origin. It is an established practice to apply the reducing agent in excess in real-life remediation operations[40] to compensate for the loss of Fe(0) due to non-dehalogenative side reactions occurring in the oxidative environment. We tested the VOCl deterioration activity of the HG sample series mixed in equimolar amount as well as in x2 and x3 excess to groundwater samples taken from the contaminated well. The reaction time was 6 hours, nZVI samples were synthesized in 2500, 5000 and 10000 ppm concentration and results are summarized in Figure 5. Deterioration efficiency percentage is calculated from the ratio of summed VOCl concentrations after 6 hours to that of the starting total VOCl concentration, thus an efficiency of 100% would correspond to the total removal of VOCl's from the water.

XXX Insert Figure 5 here please XXX

The following observations can be made from the data. Increasing the nZVI excess is beneficial for VOCl removal: regardless of the sol concentration and the synthesis method, triplicating the iron to VOCl ratio roughly doubles the dehalogenation efficiency. Performance is also significantly affected by the iron nanoparticle synthesis method: the best HG3-Fe material outperformed the worst HG1-Fe by a factor of three under identical conditions. In agreement with literature reports, $NaBH_4$ reduced samples work slightly better than $Na_2S_2O_4$ derived ones[41]. Interestingly, increasing the iron concentration from 2500 to 5000 ppm causes only a marginal efficiency improvement and increasing it further to 10000 ppm can even reduce the efficiency. A possible explanation for the 5000 ppm optimum is that

nZVI-consuming side reactions are relatively more important at low iron concentration, whereas at high iron concentration the probability of particle agglomeration increases.

Field test of HG4-Fe

O'Carroll et al. have recently reviewed the applicability of nZVI in contaminated groundwater restoration[42]. Reports specific to field scale tests are scarce but available from e.g. Quinn et al.[43] and more recently from Wei et al.[44,45], Su et al.[46] and Kocur et al.[47], Our field test was part of a large scale commercial remediation project undertaken in 2014-2015 on the south-eastern part of the Great Hungarian Plain. Semi-green sample HG4-Fe was chosen for a scaled-up field test because (i) its ORP was significantly more negative than that of all natural plant extract derived nZVI sols, (ii) it exhibited a solid overall performance in both ORP-based and GC-MS-based VOCl removal laboratory tests and (iii) it does not introduce any toxic boron compounds into the environment. A grid of injection and monitoring wells allowing access to groundwater bodies between -5 m to -30 m was established at the contaminated site. Samples were taken through silicone tubing and kept in completely filled glass vessels at 4 °C in dark until analysis. Sampling was deliberately timed for precipitation-free periods: at least 2 dry days passed before each sampling date to exclude any artifacts introduced by the dilution of groundwater by surface sources (rain or snow). Table 1. summarizes the weather conditions on all sampling and injection days.

XXX Insert Table 1 here please! XXX

The ground at the field test site was layered as follows. The topmost thin fertile soil layer (10-15 cm deep) was followed by clay to -3 m, then by sandy clay loam to -5 m. Alternating layers of sandy clay loam and muddy clay followed between -5 and -12 m and a clay body was located between -12 m and -25 m. A 0.5 m thick sandy clay layer was enclosed in the clay body at -22 m. The level of groundwater was at -5 m during the test. It is subject to ±1 m variation yearly. The pore pressure gradient in the test area was 40 $kPa \cdot m^{-1}$, however, at -12 m a local minimum was found in the pore pressure (100-180 kPa instead of 480 kPa) and this facilitated injection at this level.

The base concentration of the main pollutants (PCE (perchloroethene), TCE (trichloroethene), DCE (1,2-dichloroethene) and VC (chloroethene)) in the groundwater was determined on 09/17/2014. On 09/19/2014 more than 500 dm^3 5000 ppm HG4-Fe sol was

injected at -12 m, then the monitoring phase was started. The distance between the injection and the monitoring well was less than 5 m. HG4-Fe injection was repeated using identical process parameters on 11/26/2014 and monitoring was concluded in January 2015. Figure 6. depicts the changes in the concentration of the main VOCls in this period in this monitoring well. PCE and TCE were eliminated completely and the amount of VC and DCE was reduced below 15 $\mu g \cdot dm^{-3}$.

XXX Insert Figure 6 here please XXX

SUMMARY

We compared the reductive dehalogenation efficiency of zero valent iron nanoparticles in removing volatile chlorinated organic compounds (VOCls) from groundwater samples obtained from a real remediation target site. Completely green synthesis methods utilized plant extracts (green tea, coffee, Virginia creeper) as iron salt reducing and nanoparticle capping agents, semi-green methods utilized industrial chemicals but all reactions were carried out at ambient conditions in untreated tap water instead of resource-hungry deoxygenated solvents. Although semi-green methods yielded iron nanoparticles with smaller average diameter and better reducing abilities than green ones, the latter performed acceptably as well. The applicability of Virginia creeper extract in nZVI synthesis was reported here for the first time.

Iron nanoparticles prepared using $NaBH_4$ outperformed those made with $Na_2S_2O_4$ in ORP and VOCl deterioration tests. However, sodium borohydride is more expensive and more toxic than sodium dithionite and yields toxic boron compounds that should not be allowed into the environment. Therefore, the sustainable optimum nZVI material identified by this study was HG4-Fe, which was prepared from $FeSO_4$ and $Na_2S_2O_4$. This material was tested under field conditions at a contaminated site and was found to degrade VOCls with appreciable efficiency.

ACKNOWLEDGEMENTS

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TABLE CAPTIONS

Table 1. A summary of the meteorological conditions on the sampling and injection days of the field test.

TABLE

Table 1. A summary of the meteorological conditions on the sampling and injection days of the field test.

Date	Air temperature (°C)	Precipitation (mm)	Humidity (RH%).	Air pressure (hPa)	Wind speed ($km \cdot h^{-1}$)
09.17.2014	16 °C	0	88	1020	0
09.19.2014 (injection)	21 °C	0	41	1021	1.8
10.27.2014	4 °C	0	95	1033	3.6
11.24.2014	8 °C	0	44	1028	3.6
11.26.2014 (injection)	1 °C	0	99	1026	7.2
12.03.2014	8.0 °C	0	93	1021	9.3
12.19.2014	8.0 °C	0	81	1019	20.4
01.21.2015	6.0 °C	0.1	100	1015	3.7

FIGURE CAPTIONS

Figure 1. TEM images of nZVI samples: a) GT-Fe, b) VC-Fe, c) HG1-Fe, d) HG2-Fe, e) HG3-Fe, f) HG4-Fe. The TEM image of C-Fe was indistinguishable from that of GT-Fe, therefore, it is not shown here.

Figure 2. Oxidation/reduction potential values of nZVI sols as a function of time without a reaction partner (left panel) and with the addition of groundwater containing 1 equivalent amount of VOCl (right panel). Lines connecting the measured points are guides for the eye.

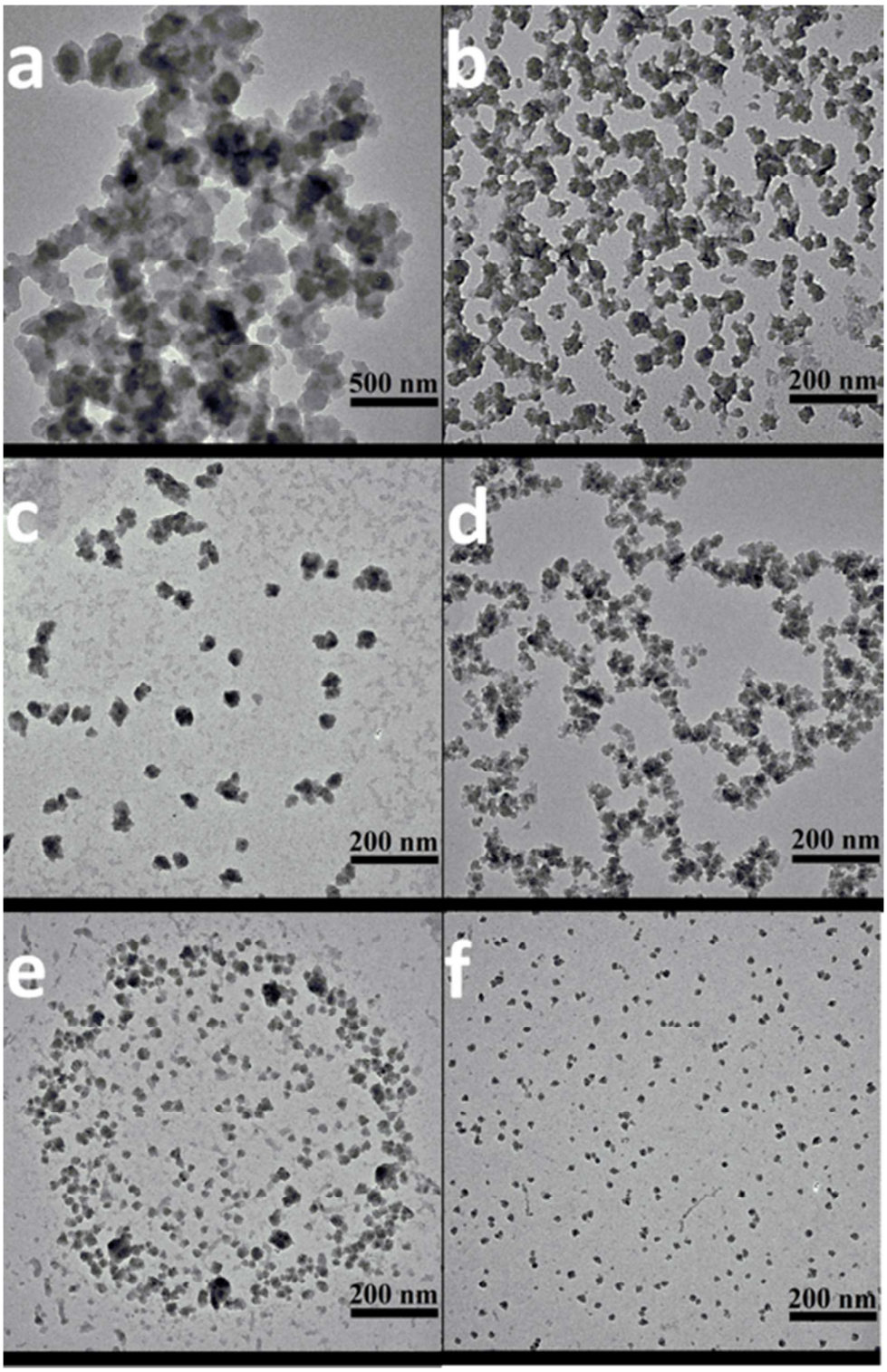
Figure 3. Efficiency of the semi-green nZVI sols in water equivalent to laboratory (black square) and in field (red circle) deoxygenation conditions, as determined from the evolution of H_2 in the reaction of nZVI and sulphuric acid.

Figure 4. Powder X-ray diffractograms of semi-green nZVI sols. Curves from bottom to top correspond to HG1-Fe to HG4-Fe, respectively.

Figure 5. Efficiency of semi-green nZVI sols applied in three different concentrations for the reductive dehalogenation of VOCl-containing groundwater. Lines connecting the measured points are guides for the eye.

Figure 6. Results of a remediation field test performed with 5000 ppm HG4-Fe nZVI sol injected into VOCl-contaminated groundwater twice. Red dots mark the injection dates, colored lines indicate the changes in the concentration of the four main pollutants (PCE: perchloroethene, TCE: trichloroethene, DCE: 1,2-dichloroethene (cis and trans combined), VC: chloroethene) in the monitoring phase.

FIGURES



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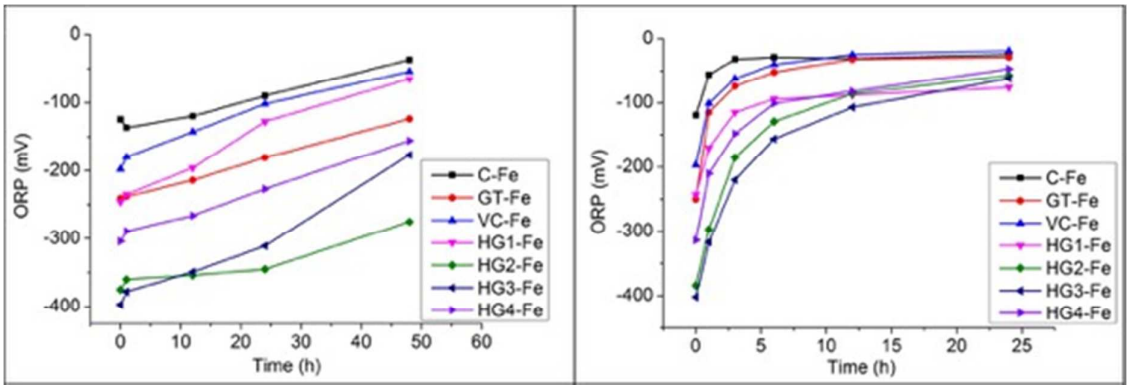

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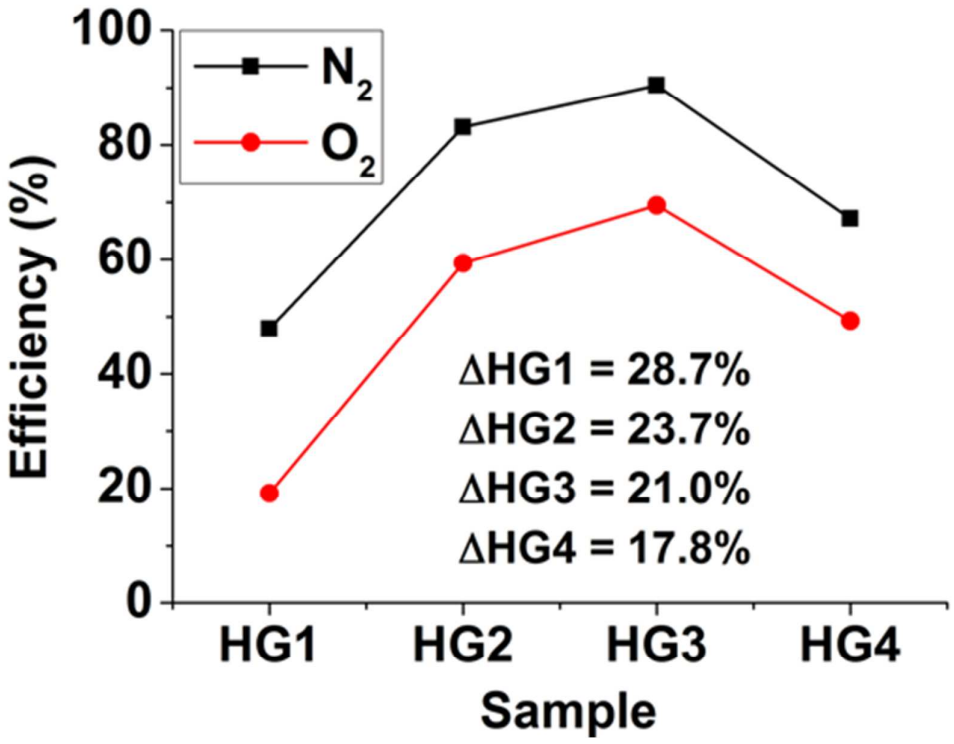

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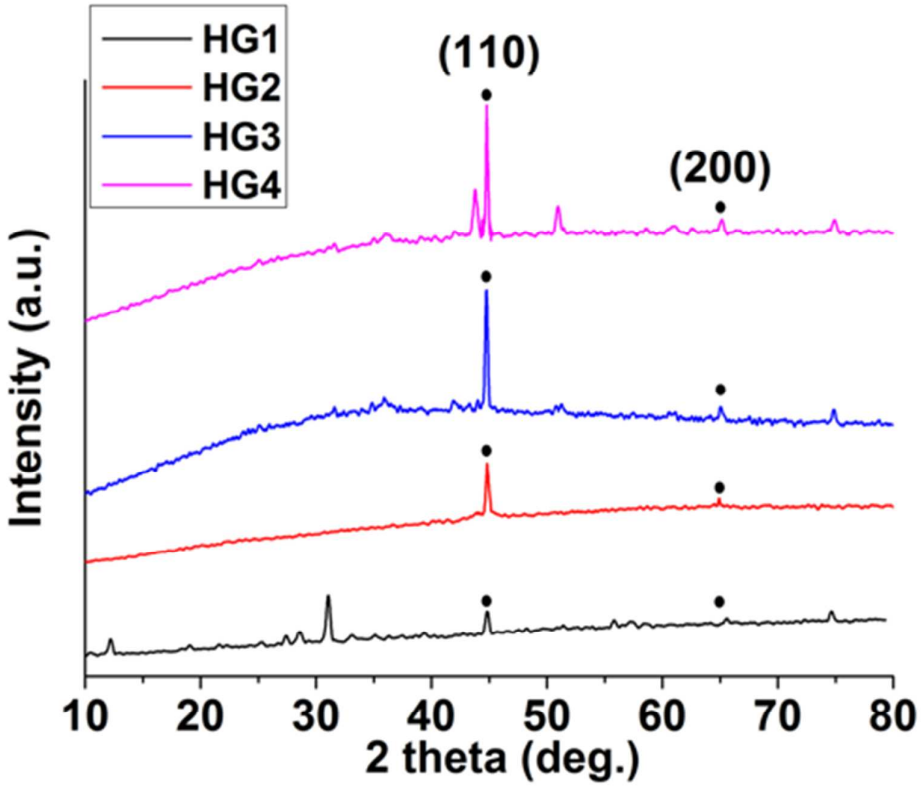

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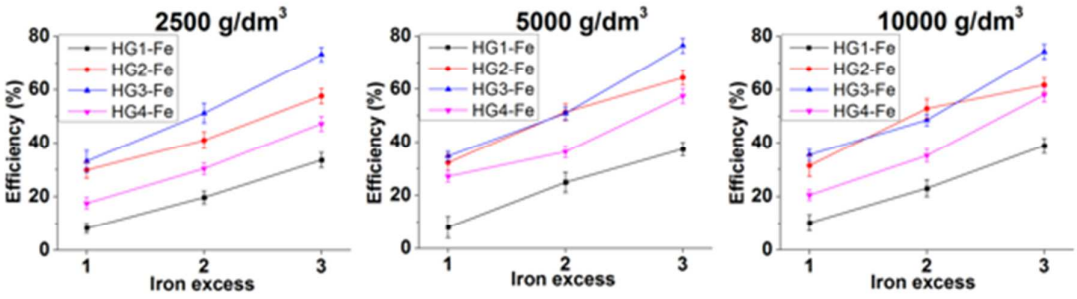

Figure 5. Efficiency of semi-green nZVI sols applied in three different concentrations for the reductive dehalogenation of VOCl-containing groundwater. Lines connecting the measured points are guides for the eye.

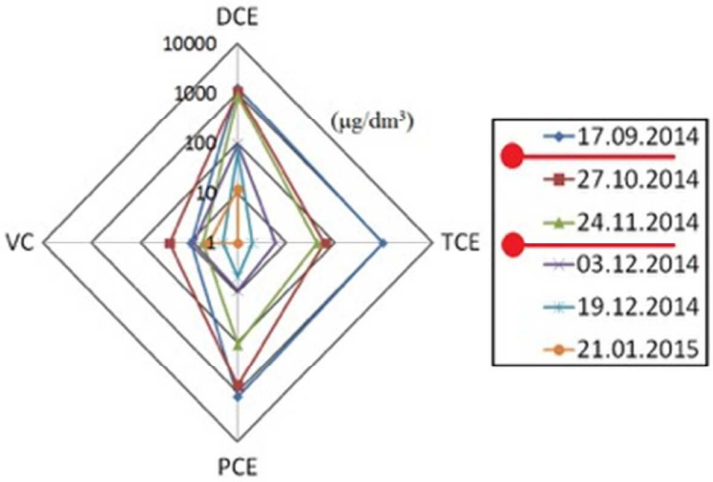

Figure 6. Results of a remediation field test performed with 5000 ppm HG4-Fe nZVI sol injected into VOCl-contaminated groundwater twice. Red dots mark the injection dates, colored lines indicate the changes in the concentration of the four main pollutants (PCE: perchloroethene, TCE: trichloroethene, DCE: 1,2-dichloroethene (cis and trans combined), VC: chloroethene) in the monitoring phase.

Environmentally benign synthesis methods of zero valent iron nanoparticles

Gábor Kozma, Andrea Rónavári, Zoltán Kónya, Ákos Kukovecz

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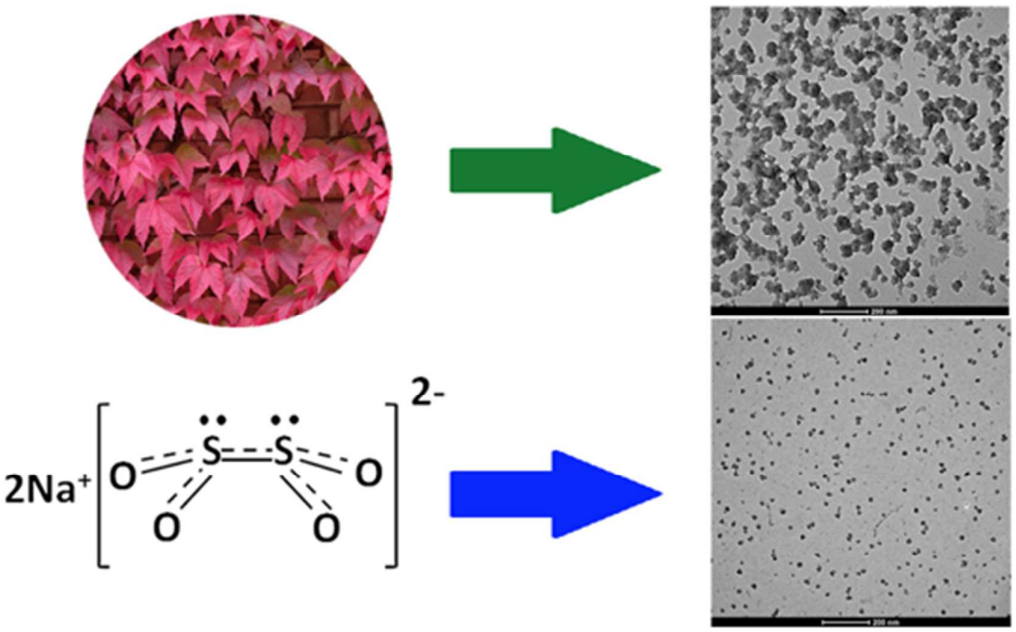

SYNOPSIS

Zero-valent iron nanoparticles synthesized by using conventional chemicals and natural product extracts are compared and their volatile chlorinated organics degradation efficiency is tested on groundwater samples obtained from an actual nanoremediation site.

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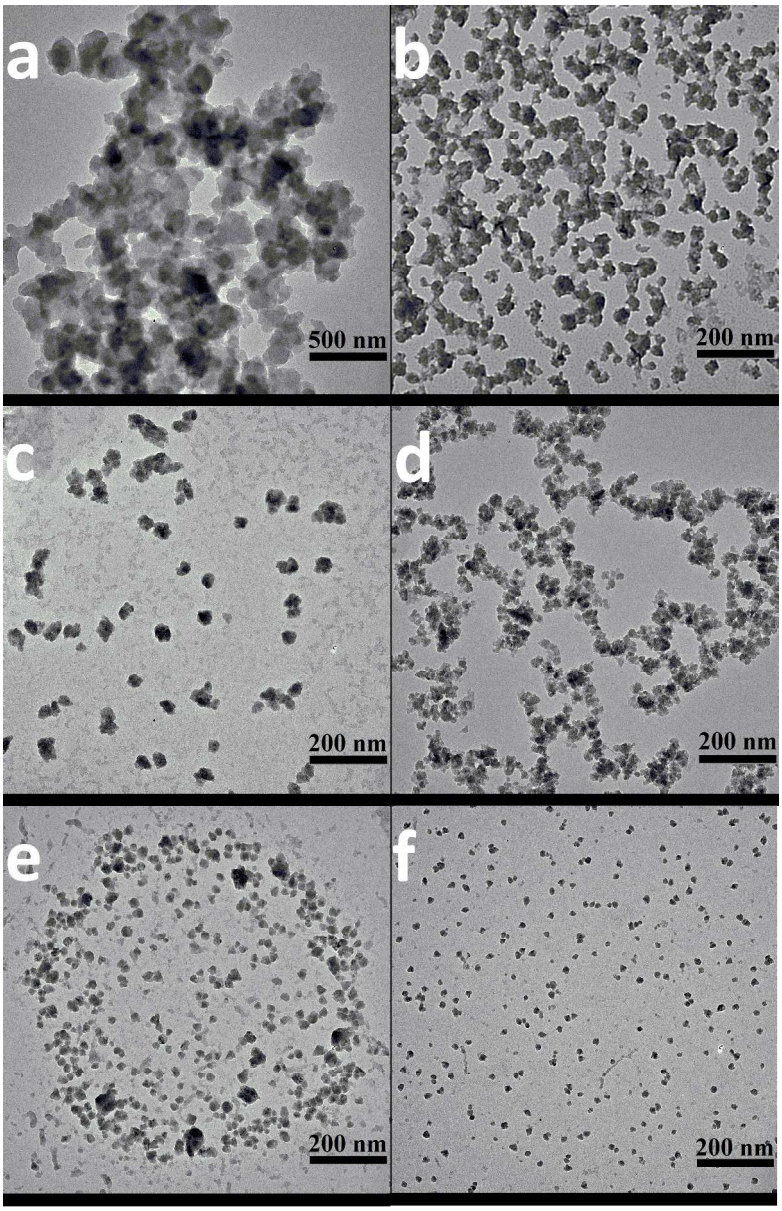

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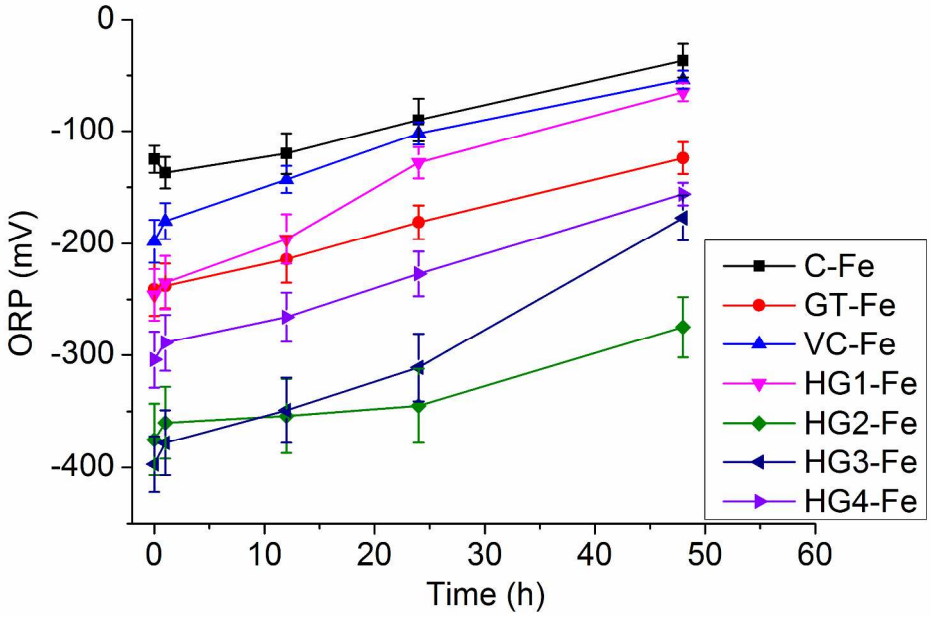

Figure 2 left panel
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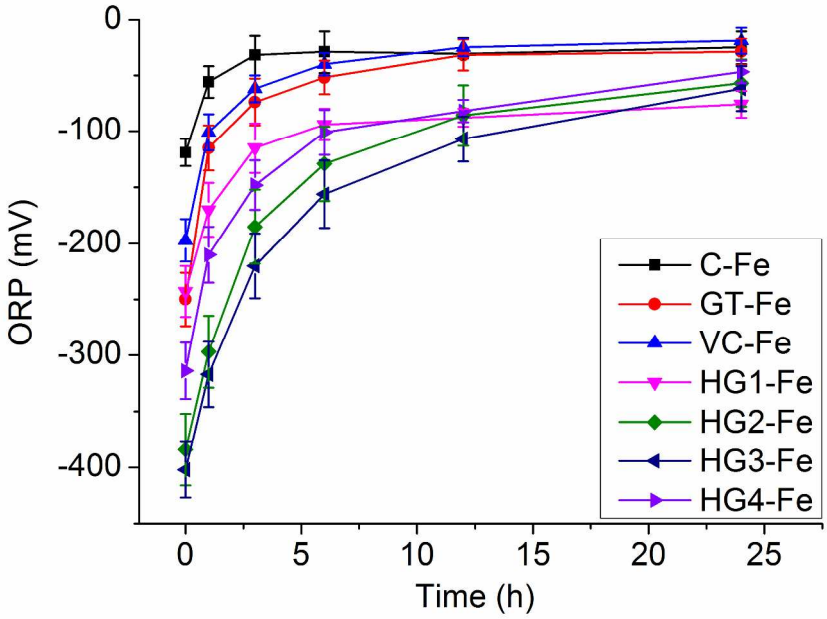

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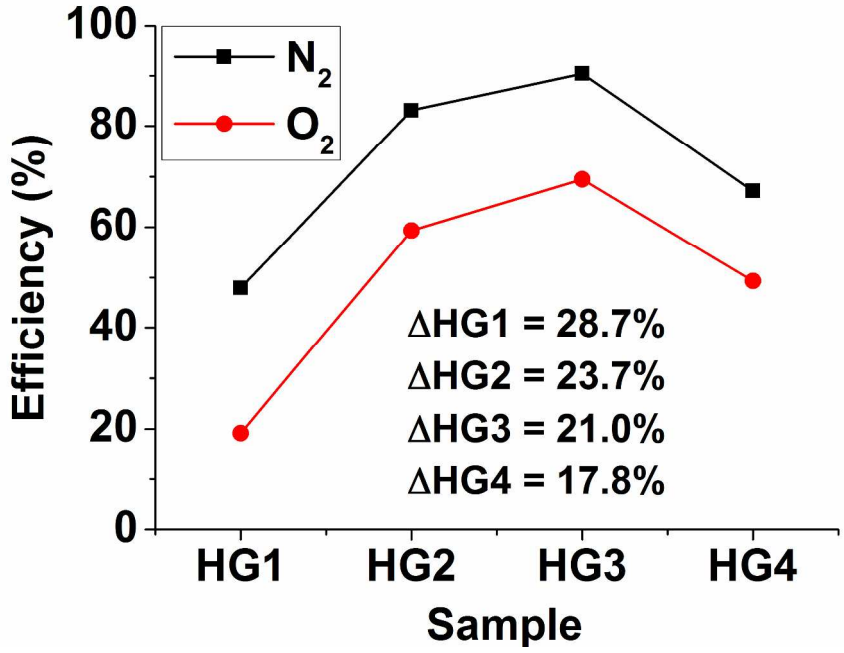

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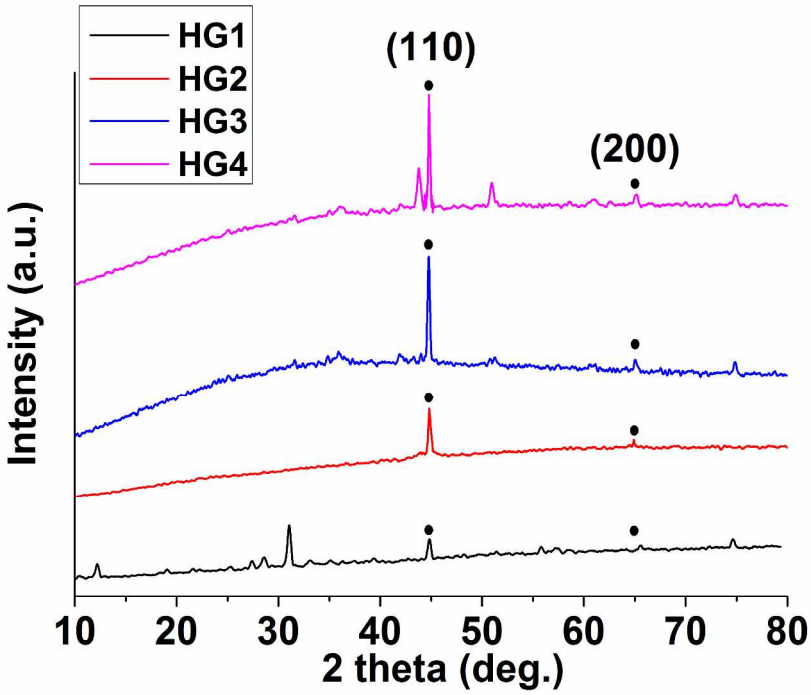

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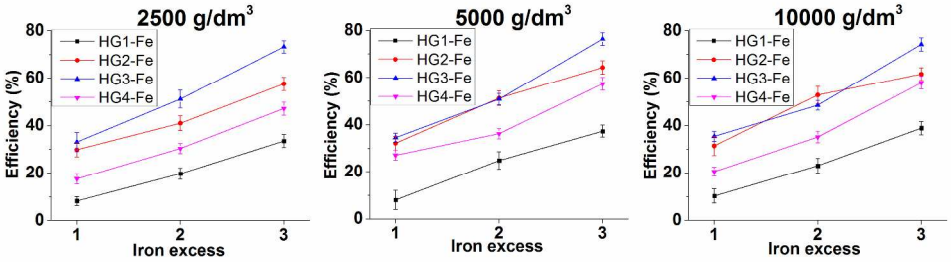

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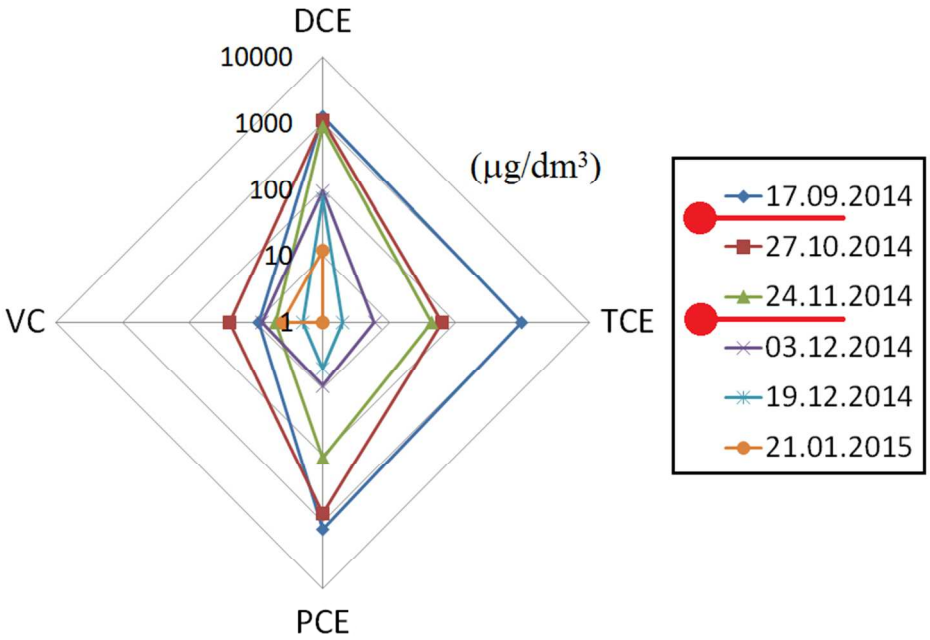

Figure 6
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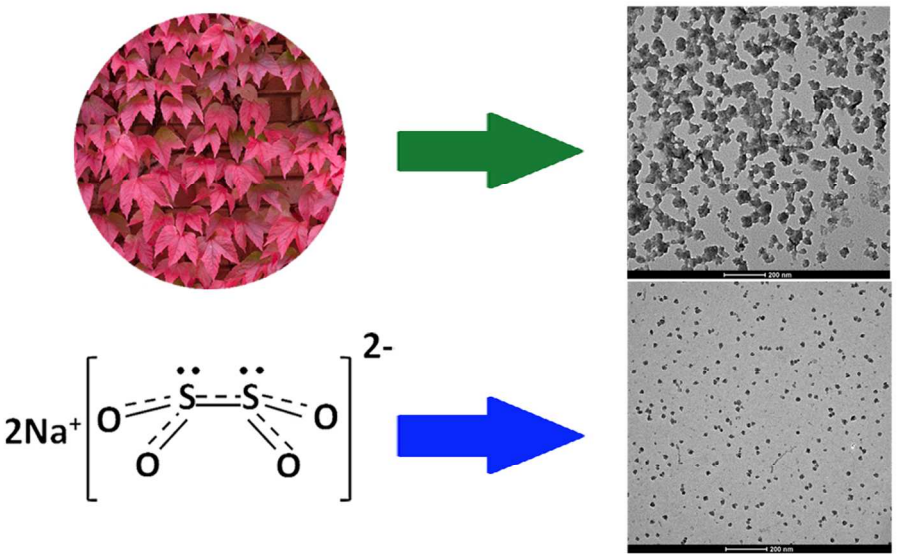

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